Novel Reworkable Fluxing Underfill for Board-Level Assembly

Zhuqing Zhang, Haiying Li, and C. P. Wong, *Fellow, IEEE*

***Abstract*—Underfills are traditionally applied for flip-chip applications. Recently, there has been increasing use of underfill for board-level assembly including ball grid arrays (BGAs) and chip scale packages (CSPs) to enhance reliability in harsh environments and impact resistance to mechanical shocks. The no-flow underfill process eliminates the need for capillary flow and combines fluxing and underfilling into one process step, which simplifies the assembly of underfilled BGAs and CSPs for SMT applications. However, the lack of reworkability decreases the final yield of assembled systems. In this paper, no-flow underfill formulations are developed to provide fluxing capability, reworkability, high impact resistance, and good reliability for the board-level components. The designed underfill materials are characterized with the differential scanning calorimeter (DSC), the thermal mechanical analyzer (TMA), and the dynamic mechanical analyzer (DMA). The potential reworkability of the underfills is evaluated using the die shear test at elevated temperatures. The 3-point bending test and the DMA frequency sweep indicate that the developed materials have high fracture toughness and good damping properties. CSP components are assembled on the board using developed underfill. High interconnect yield is achieved. Reworkability of the underfills is demonstrated. The reliability of the components is evaluated in air-to-air thermal shock (AATS). The developed formulations have potentially high reliability for board-level components.**

***Index Terms*—Assembly, material properties, reworkable, reliability, underfill.**

I. Introduction

UNDERFILLS are traditionally applied for flip-chips to enhance the reliability through redistributing the thermal mechanical stress on the solder joint generated by the mismatch of the coefficient of thermal expansion (CTE) between the silicon chip and the organic substrate [1], [2]. Recently, there has been an increasing use of underfill for board-level assembly including ball grid arrays (BGAs) and chip scale packages (CSPs). BGAs and CSPs were first designed to eliminate the need for encapsulation, to be surface mount technology (SMT) processes compatible, and to have good handling properties. However, it has been found that dynamic loading induced by mechanical vibration and impact shock has become the one of the major reliability detractors for these packages [3], [4], especially in the hand-held, telecommunication applications. In addition, although board-level reliability of the BGAs and CSPs is typically not of concern because of the relatively mild environment temperature fluctuations, avionics, automotive, and telecommunication environments can be more rigorous. Improved reliability of the board-level components is needed for these applications [5]. Therefore, underfill encapsulation is increasingly used for enhancing reliability in harsh environments and impact resistance to mechanical shocks for board-level assembly. However, the use of underfill adds to the process steps of board-level assembly. The dispensing and the curing of the underfill have to be done separately. Hence, underfill in BGAs and CSPs diminishes the original purpose of the design of these packages to be SMT assembled and significantly adds to the cost of the board-level assembly. On the other hand, reworkability is very important for board-level assembly because the current electronic system usually integrates many electronic devices or discrete components onto a multilayer printed wiring board (PWB). The rework process has been studied and demonstrated with board-level components like BGAs and CSPs without underfill [6]–[8]. However, most underfills are epoxy-based thermosetting resins that are not reworkable. The inability to replace defective board-level components that are underfilled renders the whole board useless. For these reasons, the use of underfill in the board-level assembly becomes a dilemma.

The invention of no-flow underfill eliminates the need for capillary flow and combines underfill curing and solder reflow into one step [9], [10], which simplifies the assembly of flip-chips, as well as underfilled BGAs and CSPs, for SMT applications. Although the addition of silica fillers into the no-flow underfill has been difficult because the filler entrapment causes an interconnect yield problem [11], the thermal mechanical stress on the solder joint is not as significant for the robust BGAs and CSPs, which tend to have larger solder bumps and coarser pitch, as for the flip-chips which usually have high I/O counts and smaller solder joints; therefore the high CTE of the no-flow underfill can be tolerated in the application of the board-level components. The idea of reworkable underfill has been around for a long time; both chemically and thermally reworkable underfill materials have been developed and the rework process has been demonstrated [12]–[15]. The novel approach to combine the no-flow underfill and the reworkable underfill together was pioneered by Wang *et al.* [16], who demonstrated the reworkability of the no-flow underfill by incorporating either thermally degradable epoxy or thermally degradable additives into a typical no-flow underfill. However, the effect of the epoxy degrading during solder reflow might have an impact on the material properties of the underfill. This was not studied in the previous work. In addition, the developed no-flow underfill was based on cycloaliphatic epoxy and anhydride chemistry, which possessed a high Tg, high modulus, and was brittle in nature.

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TABLE I
DETAILED FORMULATIONS OF THE UNDERFILLS IN THE STUDY

	Epoxy	Hardener	Catalyst
Formulation C	EPON 862 (1)	LBR-6 (0.48)	C_{11}-CNS (0.01)
Formulation D	EPON 862 (1)	MHHPA (0.78)	C_{11}-CNS (0.01)
Formulation E	EPON 862(1)	MHHPA (0.59), LBR-6 (0.12)	C_{11}-CNS (0.01)
Formulation E1	EPON 862 (1), EPON 58034 (0.25)	MHHPA (0.68), LBR-6 (0.14)	C_{11}-CNS (0.01)

It cannot provide the required impact resistance for board-level components.

In this paper, epoxy underfills with mixed hardeners of anhydride and phenolic resin are developed and investigated for the application of no-flow underfill for board-level assembly. The phenolic resin provides fluxing capability to facilitate solder joint formation, as well as rework capability due to its low crosslinking density. Rubber modified epoxy resin is used to improve the impact resistance of the underfill.

II. EXPERIMENTAL

A. Materials

The materials used in the underfill formulations included different epoxy resins, an anhydride hardener, a phenolic hardener, and a latent catalyst. The epoxy resins used in this study were EPON 862 and EPON 58 034 from Shell Chemical Company. The epoxy equivalent weight (EEW) values of the two epoxy resins were 171 and 290 g/mol, respectively. The anhydride hardener was methylhexa-hydrophthalic anhydride (MHHPA) from Lindau Chemicals, Inc. Its hydroxyl equivalent weight (HEW) was 168 g/mol. The phenolic hardener was LBR-6 from Sumitomo Plastics America, Inc. Its HEW was 102 g/mol. The catalyst was 1-cyanoethyl-2-undecylimizolium trimellitate (C11Z-CNS) from Shikoku Chemicals Corporation. The detailed formulations are listed Table I. The relative amount of each ingredient is listed in parentheses.

B. Characterization

The curing behavior of the formulations was characterized using a modulated differential scanning calorimeter (DSC) by TA Instruments, Model 2920 at a heating rate of 5 °C/min. The glass transition temperature (Tg) of the cured sample was measured using the DSC. The coefficient of thermal expansion (CTE) of a cured sample was measured on a thermomechanical analyzer (TMA) by TA Instruments, Model 2940. The sample was heated in the TMA furnace at 5 °C/min from room temperature to 250 °C. A dynamic mechanical analyzer (DMA) by TA Instruments, Model 2980, was used to study the dynamic moduli and the damping property of a cured sample. The measurement was performed in a single cantilever mode under 1 Hz sinusoidal strain loading. The sample was heated at 3 °C/min in air from room temperature to 250 °C to observe the change of the storage modulus (E'), loss modulus (E"), and loss angle $(\tan\delta)$ with respect to temperature. To study the damping property of a sample at room temperature, a frequency sweep of the DMA was performed with the frequency ranging from 0.1 to 100 Hz. Each sample was scanned five times in this range.

Adhesion of the underfill formulations to the solder mask-coated FR-4 substrate was conducted in shear mode using a bond tester (Model 550–100 K, Royce Instruments). The substrate was pre-cleaned using isopropanol and dried at 120 °C for 2 h. A heating stage was used on the bond tester to control the temperature of the substrate. Samples were prepared using 2×2 mm dies with silicon nitride passivation. Spherical glass beads of 75 μm diameter were added into the formulation to ensure consistent gap size.

To study the mechanical properties of the underfill samples, flexure tests were performed using a universial testing machine (UTM) by Instron. The tests were conducted at room temperature. The loading speed was 1 mm/min. The maximum stress and the strain at break of each specimen were recorded and the flexure modulus was calculated. For each sample, six specimens were prepared for the average as reported.

C. Assembly

To evaluate the process capability of the developed underfill formulations, CSP components with daisy-chained eutectic SnPb bumps were used. There were 98 bumps per component and they were daisy-chained into three channels, through which the electrical continuity could be tested. The diameter of the bumps on the CSP components is 300 μm with a pitch size of 500 μm. There were eight sites on each substrate, two of which were assembled without underfill. An epoxy type flux was used and no cleaning procedure was conducted after assembly. The other six sites were assembled using the developed no-flow underfill formulations. A K&S Assembly System was used to place the components onto the board and a seven-zone BTU reflow oven was used with the reflow profile as shown in Fig. 1.

D. Rework

The rework process was performed on a Freedom HGR 2000 rework station by Conceptronic. The developed rework process consisted of heating the substrate to the melting point of the SnPb solder and removing the CSP components from the substrate. The underfill residue after component removal was cleaned using a horsehair brush with isopropyl alcohol (IPA). Only two components on the substrate were reworked.

E. Reliability

After rework process, the remaining six components on the substrate were subjected to air-to-air thermal shock (AATS) in a Thermotron Environmental Test Chamber. The test condition was a 20-min cycle from -55 to 125 °C, with a 10-min dwell at both cold and hot. The electrical continuity of each channel of the components was tested every 100 cycles.

III. RESULTS AND DISCUSSION

A. Formulation Design

Most epoxy-based underfills are thermosetting polymers that are crosslinked upon heating. Because of this high crosslinking density, the materials cannot flow even when heated above their Tg. Thermoplastic polymers, on the other hand, become flowable at elevated temperatures, usually 40–60 °C higher than

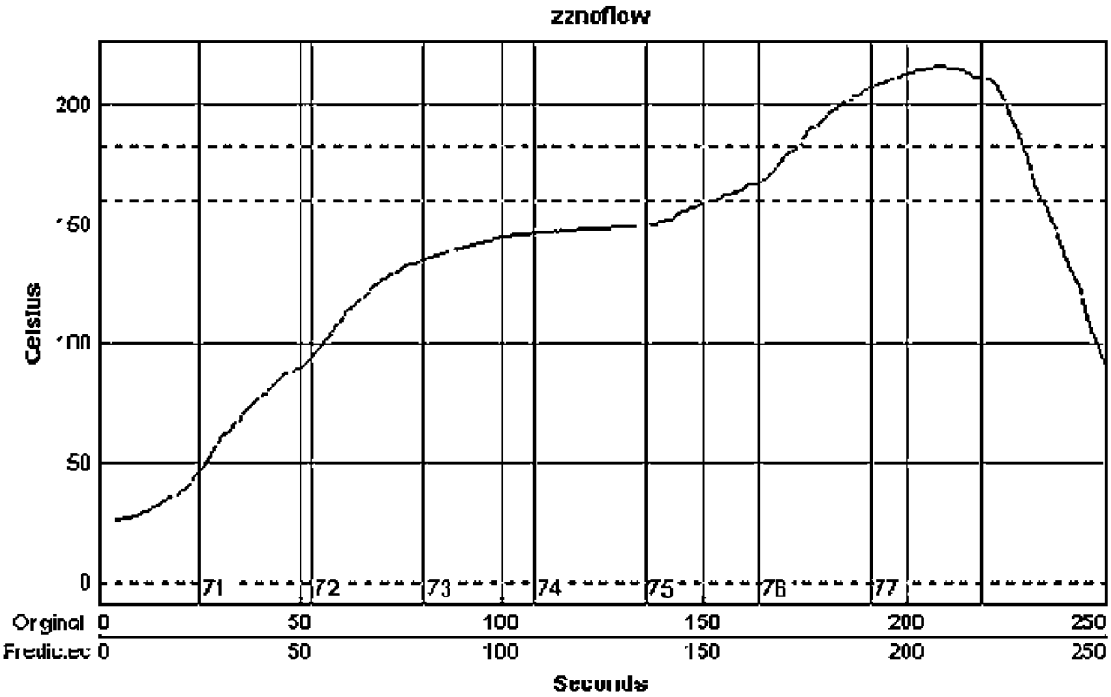

Fig. 1. Reflow profile used for CSP components assembly.

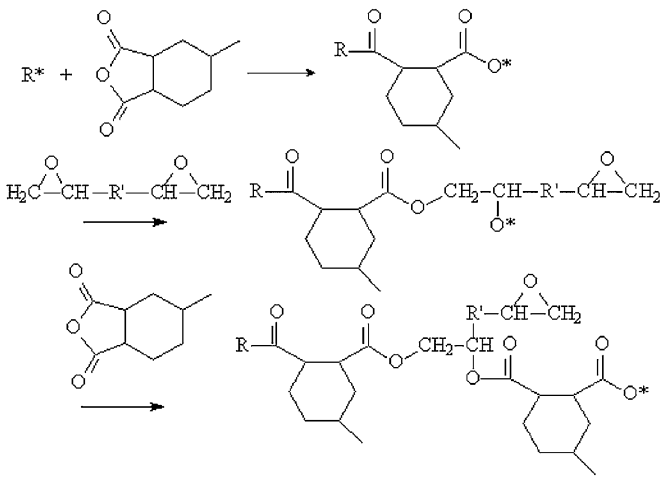

Fig. 2. Reaction mechanism of epoxy/anhydride curing.

Tg, and are ideal reworkable materials. However, most thermoplastic polymers do not possess good adhesion to the substrates and therefore the reliability is a concern. Our previous work on the nonanhydride no-flow underfill has shown that by choosing phenolic resin with low functionality, epoxy/phenolic resin-based formulations possess low crosslinking compared with epoxy/anhydride based formulations. They also display intrinsic fluxing capability, good adhesion strength, high fracture toughness, and good reliability during thermal cycling [17].

The difference between the epoxy/anhydride system and the epoxy/phenolic system can be explained by the reaction mechanism as shown in Figs. 2 and 3. In Fig. 2, R* is the nucleophilic reaction center, usually an initiator or a catalyst, which reacts with anhydride first to open the anhydride ring. The anhydride with the reaction center then reacts with the epoxide to open the epoxy ring and to transfer the reaction center to the epoxy. Since one epoxy molecule with two epoxide groups can react with four anhydrides, the functionality of epoxy is four. On the other hand, when epoxy reacts with phenolic resin as shown in Fig. 3, one epoxy molecule reacts with only two phenol groups. The functionality of the epoxy is therefore 2. The LBR-6 used in this study is a special designed phenolic resin with an average functionality of 2.4. If both the two components have a functionality of 2, it is known that the resulting polymer is linear. Therefore, the epoxy/phenolic system in study is expected to be slightly cross-linked with a high DOC at gelation.

Formulation C and Formulation D are two underfills with the same epoxy resin and catalyst but difficult hardeners. Formulation C uses phenolic resin while Formulation D contains anhydride. Fig. 4 shows their curing behaviors. It can be seen that both formulations possess latent curing capability for the application of no-flow underfill.

To evaluate the reworkability of the underfill, a die shear test was performed using solder mask coated FR-4 at different temperatures. As shown in Fig. 5, Formulation C displays high adhesion strength at room temperature. With the increase in temperature, the adhesion toward the solder mask decreased significantly, which can provide potential reworkability. On the other hand, the adhesion of Formulation D does not decrease too much even after reaching its Tg (120 °C). The drawbacks of the epoxy/phenolic resin based formulations are their low Tg (75 °C for Formulation C) and their high viscosity at room temperature, which makes underfill dispensing very difficult. Hence, mixed hardeners are used in this study. Formulations E and E1 contain both anhydride and phenolic resin as the hardeners. Rubber modified epoxy resin was added in Formulation E1 to improve its damping property. Fig. 4 also shows the curing behavior of these two formulations in comparison with Formulations C and D. As can be seen in the figure, both formulations have two curing peaks indicating the curing of epoxy/anhydride

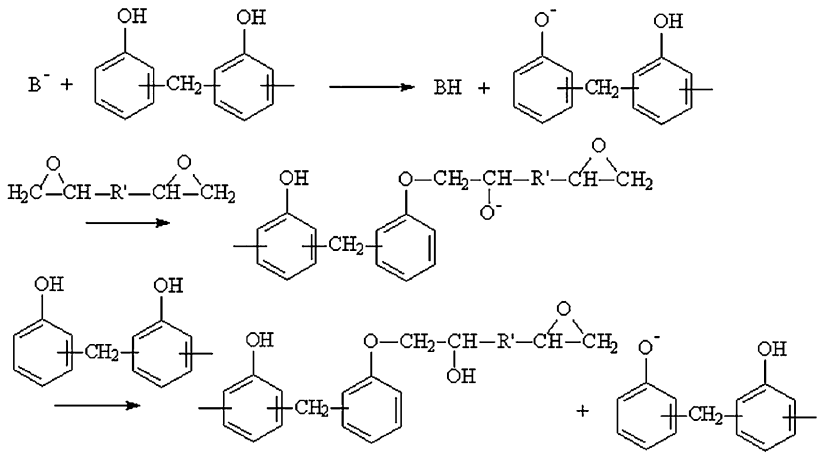

Fig. 3. Reaction mechanism of epoxy/phenolic curing.

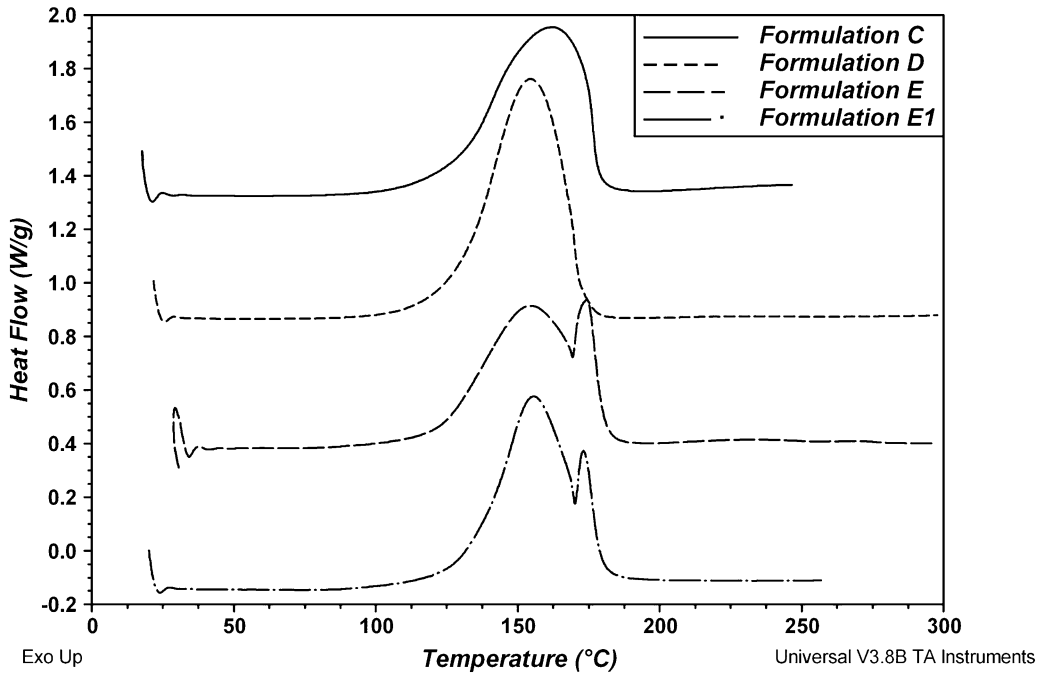

Fig. 4. Curing behavior of formulations in study.

and epoxy/phenolic resin. The following characterization and assembly are based on these two formulations.

B. Material Property Characterization

1) Adhesion to Solder Mask: As discussed earlier, adhesion of the underfill to the solder mask coated FR-4 substrate at different temperature can be an indication of the reworkability of the underfill. Three formulations, Formulation E, Formulation E1, and Formulation A which is a typical no-flow underfill based on the epoxy/anhydride/polyol fluxing agent were compared in terms of their adhesion toward the solder mask. Fig. 5 shows that the apparent adhesion strength of Formulations E and E1 decreases significantly with increasing temperature while the decrease in adhesion of Formulation A is not as much at high temperature. Notice that Formulation E has a comparable Tg (110 °C) to Formulation A (120 °C). Both Formulations E and E1 have comparable or even better adhesion strength than Formulation A at room temperature, providing good reliability. At elevated temperatures, the decrease of adhesion of the underfill toward the substrate can provide good reworkability for board-level components reparation.

2) Mechanical Properties: A Flexure test in 3-point bending mode was performed for these two underfill formulations compared with the typical no-flow Formulation A. The results are shown in Fig. 6. As can be seen, these three underfills have similar flexure modulus and maximum stress. However, the strain at break of Formulations E and E1 is considerably higher than that of Formulation A, indicating better fracture toughness that is needed for impact resistance. Fig. 7 shows the results of a DMA frequency sweep experiment. Usually high $\mathrm{Tan}\delta$ indicates good damping property. Both Formulation E and E1 displayed better damping property as compared with Formulation A, especially Formulation E1, which contains rubber-modified

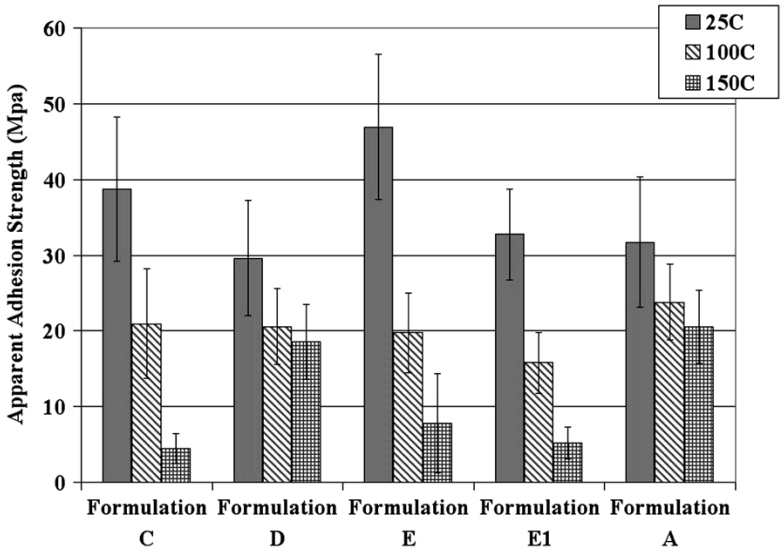

Fig. 5. Adhesion strength of formulations in study at different temperatures.

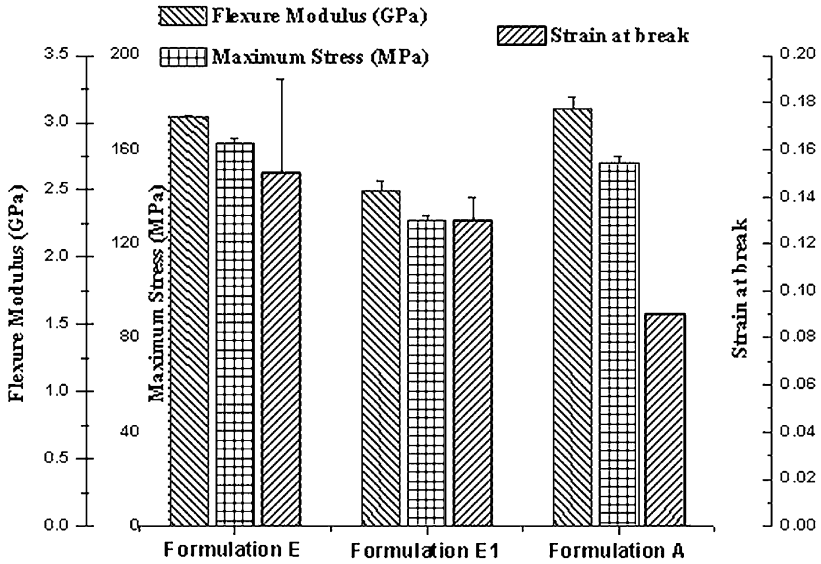

Fig. 6. Flexure modulus, maximum stress, and strain at break for the three underfills.

epoxy that provides flexible segment in the cured resin. As indicated by their mechanical properties, the developed no-flow underfills possess good impact resistance, which is desirable for the protection of board-level components.

3) Thermomechanical Properties: The thermomechanical properties of the developed underfills were characterized using the DMA and the TMA. Figs. 8 and 9 show the storage modulus and the thermal expansion of Formulation E and E1, respectively. Formulation E displayed better properties including higher modulus, higher Tg, and lower CTE, promising good reliability for board-level components.

C. Assembly and Rework

The assembly of the CSP components was carried out using a typical SMT process with flux/underfill dispensing, pick and placement, and solder reflow. Sites A and B were assembled using an epoxy type flux without flux cleaning. The underfills used in the assembly are shown in Table II, together with the assembly yield. The components assembled with Underfill E1 achieved a 100% yield based on the electrical continuity of each channels of the components. The components with Underfill E had a lower yield as can be seen from the table. The reason for this is still under investigation. Sites G and H were reworked after assembly. Fig. 10 shows a picture of Site H after rework. There was some epoxy residue left on the bonding site, indicating a bulk failure of the underfill due to the flow of a low cross-linked polymer. The epoxy residue can be cleaned using IPA.

Another board was assembled using the developed underfills for rework and reassembly. All the sites were reworked, cleaned in IPA, and replenished with soldering. Fig. 11 shows the pictures of a replenished site after rework, and after reassembly of the CSP component on the reworked site. A 100% yield was achieved with Formulation E1 while the yield with Formulation E was less than perfect. Careful observation under the optical microscope indicated no damage to the solder mask as shown

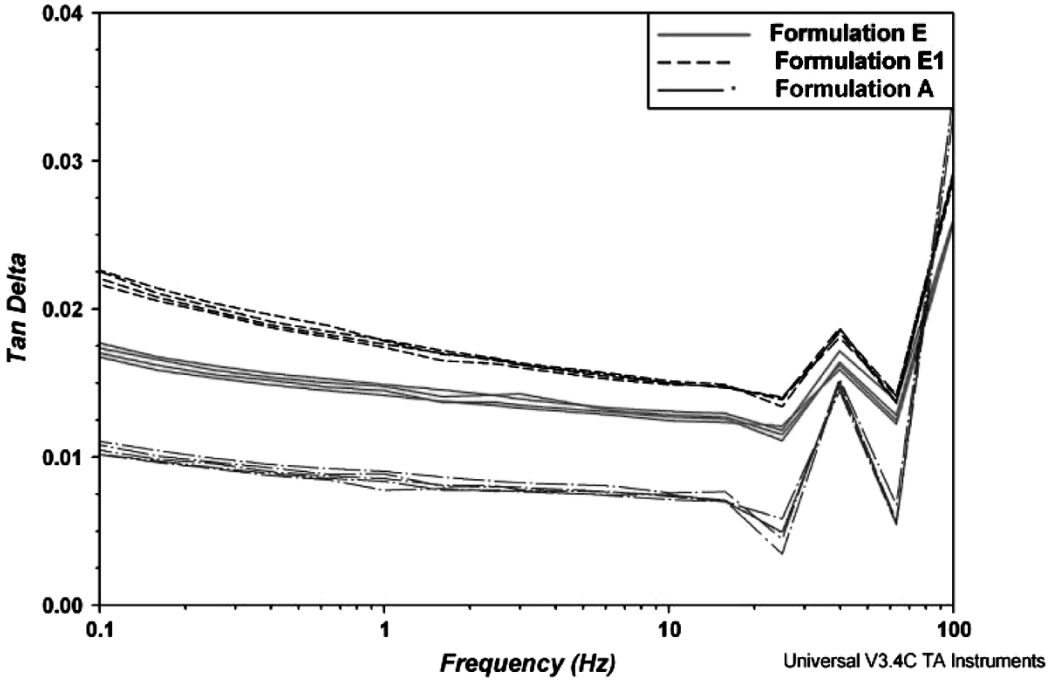

Fig. 7. Tanδ of the three underfills as a function of frequency.

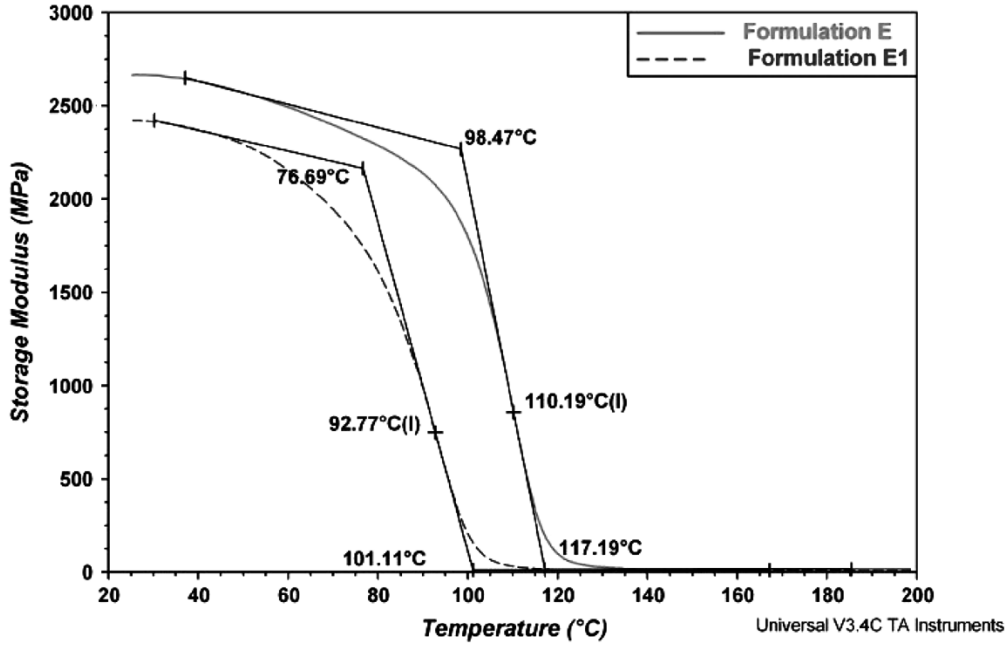

Fig. 8. Storage modulus of the developed underfills as a function of temperature.

in the close view in Fig. 11. A picture of a new site is shown for comparison.

D. Reliability

The reliability of the CSP components during air-to-air thermal shock was recorded and listed in Table III. The AATS was stopped after 1600 cycles. The components on Sites A and B failed early during the reliability test because the remaining flux on the substrate decomposed and caused outgassing as can be observed in Fig. 12. Therefore, in the conventional assembly process, flux cleaning is indispensable for achieving high reliability of the components. The flux cleaning adds to the process steps and assembly cost, while in a no-flow underfill process, fluxing cleaning is eliminated. Components on Site E and F were assembled using Formulation E1. They showed reasonable reliability and consistent yield. Components on

TABLE II
ASSEMBLY YIELD FOR THE CSP COMPONENTS

Site	Underfill	R1	R2	R3
A	None	✓	✓	✓
B	None	✓	✓	✓
C	E	✓	×	×
D	E	✓	×	✓
E	E1	✓	✓	✓
F	E1	✓	✓	✓
G	E	✓	×	×
H	E1	✓	✓	✓

√denotes failure; ×denotes pass.

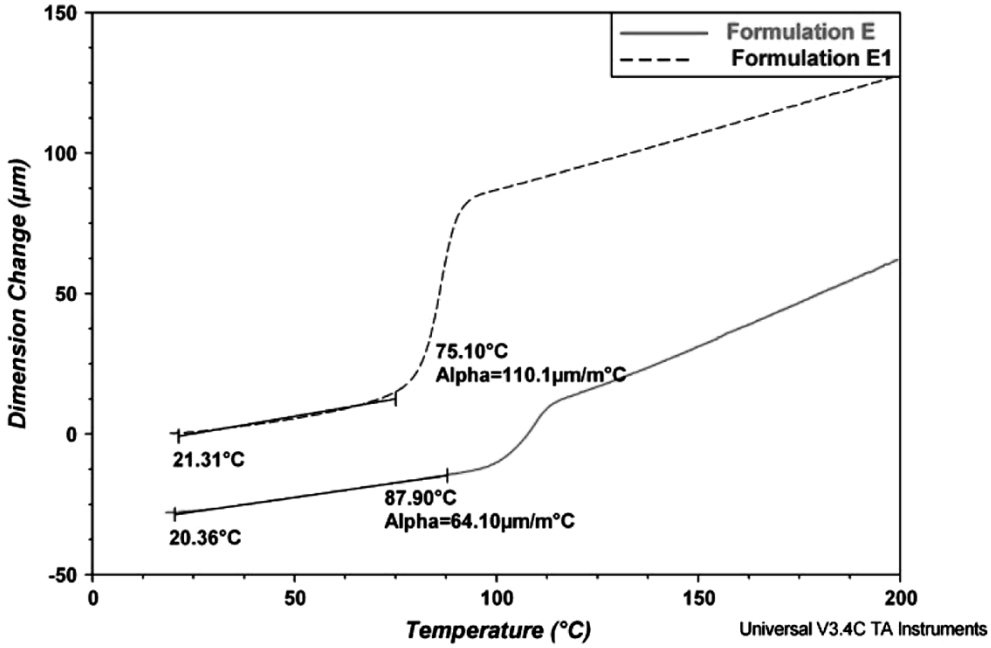

Fig. 9. Thermal expansion behavior of the developed underfills.

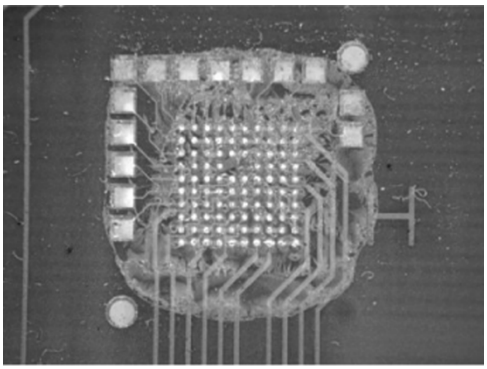

Fig. 10. A picture of Site H after rework.

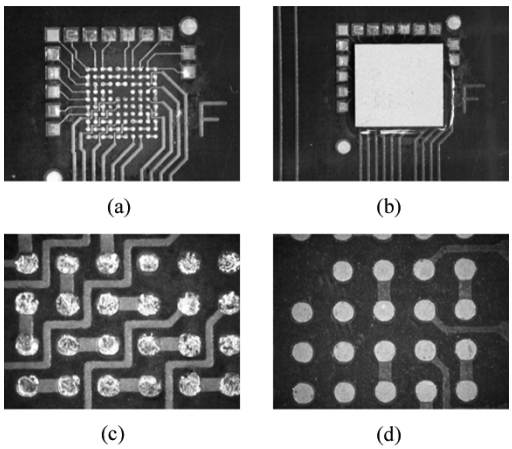

Fig. 11. Rework and reassembly of Site F. (a) Site F after rework. (b) Site F after reassembly. (c) Close view of reworked site. (d) New site for comparison.

TABLE III
RELIABILITY OF THE CSP COMPONENTS IN AATS

Site	Underfill	R1	R2	R3
A	None	**1400**	**200**	**800**
B	None	**1600**	**200**	**700**
C	E	**1600**	×	×
D	E	**1600**	×	**1600**
E	E1	**1600**	**1300**	**1600**
F	E1	**1300**	**1600**	**1600**
G	E	**RW**	**RW**	**RW**
H	E1	**RW**	**RW**	**RW**

Note: reliability test was stopped after 1600 cycles

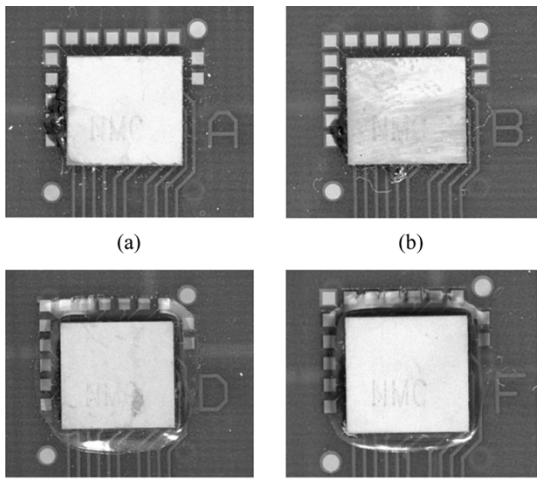

Fig. 12. Photos of the components after 1300 cycles of AATS. (a) Site A. (b) Site B. (c) Site D. (d) Site F.

Sites C and D were assembled using underfill E. Although they had some yield issues, the potential reliability is very good. As indicated in the previous material characterization, Formulation E possesses desirable properties for high reliability. Up to 1600 cycles of AATS that were conducted, those yielding interconnect joints all survived. If the assembly yield issue can be solved, Formulation E will be a desirable no-flow underfill for board-level assembly. The photos of the components on Site D and E are also shown in Fig. 13. No underfill fillet cracking was observed.

IV. Conclusion

Two underfill formulations were developed for no-flow underfill for board-level assembly applications. The material properties were characterized and the results indicated that these two underfills can provide reworkability, high impact resistance, and good reliability for board-level components, compared with a typical no-flow underfill material. CSP components were assembled onto a substrate using the SMT process with flux or in-house developed underfills. Components assembled with Formulation E1 demonstrated a 100% interconnect yield. The rework process was conducted and both underfills showed good reworkability. New components were assembled onto the reworked site and good yield was achieved. The reliability of the components was tested using air-to-air thermal shock. Components assembled with flux failed early due to the decomposition of the remaining flux. Components assembled with Formulation E1 showed reasonable reliability in AATS. Formulation E showed potential high reliability; however, the process needs to be optimized for a high interconnect yield.

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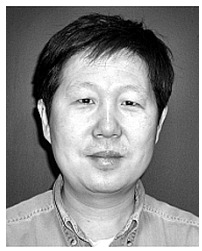

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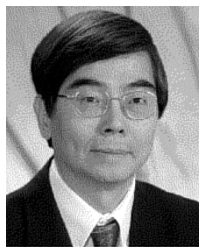
After receiving the B.S. degree, he served as a Polymer Engineer in industry for ten years and received the Third Award of the Light Industry Ministry of China for the Progress in Science and Technology in 1989 and 1991. He was nominated as one of the finalists for ICI Student Award in Applied Polymer Science in 2000. He has authored and coauthored 10 journal papers, more than 20 proceeding articles, and four U.S. patents. Currently, he is working as a contract researcher with GE Global Research Center, Niskayuna, NY.



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After his doctoral study, he was awarded two years as a Postdoctoral Scholar at Stanford University, Stanford, CA, with Prof. Henry Taube. He joined AT&T Bell Laboratories, PA, in 1977 as Member of Technical Staff. He was elected an AT&T Bell Laboratories Fellow in 1992. He is a Regents Professor with the School of Materials Science and Engineering and a Research Director at the NSF-funded Packaging Research Center, Georgia Institute of Technology (Georgia Tech), Atlanta. He holds over 40 U.S. patents, numerous international patents, and has published over 400 technical papers and 400 keynotes and presentations in related areas. His research interests lie in the fields of polymeric materials, high Tc ceramics, materials reaction mechanism, IC encapsulation, in particular, hermetic equivalent plastic packaging, electronic manufacturing packaging processes, flip-chip underfill materials, high K, high Q embedded passives, interfacial adhesions, PWB, SMT assembly, and components reliability.

Dr. Wong received the AT&T Bell Laboratories Distinguished Technical Staff Award in 1987, the AT&T Bell Fellow Award in 1992, the IEEE Components, Packaging and Manufacturing Technology (CPMT) Society Outstanding and Best Paper Awards in 1990, 1991, 1994, 1996, 1998 and 2002, the IEEE Technical Activities Board Distinguished Award in 1994, the 1995 IEEE CPMT Society's Outstanding Sustained Technical Contribution Award, the 1999 Georgia Tech Outstanding Faculty Research Program Development Award, the 1999 NSF-Packaging Research Center Faculty of the Year Award, the 1999 Georgia Tech Sigma Xi Faculty Best Research Paper Award, the University Press (London, UK) Award of Excellence, and was elected a member of the National Academy of Engineering in 2000. He served as the Technical Vice President (1990 and 1991), and President (1992 and 1993) of the IEEE CPMT Society.